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A selective fluorescent sensor for Cu(II) ion in ethanol and acetone based on BODIPY

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RESEARCH ARTICLE

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ABSTRACT

A selective fluorescent sensor for Cu(II) ion in ethanol and acetone based on boradiazaindacene (BODIPY) has been studied. The selectivity towards Cu(II) ion is good over Ag(I), Cd(II), Fe(III), Hg(II), Ni(II), Pb(II), and Zn(II) ions, only Fe(III), Hg(II) and Ni(II) ions showed a slight interference. The solution showed strong fluorescence intensity after addition of triethanolamine, indicating that the Sensor 1-Cu(II) complex could be reversed by triethanolamine.

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1. Introduction

The development of fluorescent molecular sensors for metal ions, especially for cations with biological interest, has always been of particular importance and usually involves the design and synthesis of molecules containing binding sites and a signaling unit able to display selective changes in fluorescence emission intensity upon guest binding [1-6]. More specifically, sensors directed toward the detection and measurement of divalent copper has enjoyed the particular attention.

Copper is the third most abundant essential trace element in the human body and plays a significant role in many fundamental physiological processes in organisms [7,8]. However, it is toxic at higher concentration level, for example, the accumulation of Cu(II) in the liver and kidney may cause gastrointestinal disease, Wilson disease, hypoglycemia, dyslexia and infant liver damage [9,10]. In particular, exposure to a high level of copper even for a short period of time can cause gastrointestinal disturbance, and long-term exposure causes liver or kidney damage [11], as a result of its ability to displace other metal ions that act as cofactors in enzyme-catalyzed reactions [12,13]. Thus, copper, on one hand, is important for life but, on the other hand, is highly toxic to organisms. For these reasons, the development of fluorescent sensors has been receiving lots of attention in last decade because of their simplicity and sensitivity [14]. Therefore, a number of fluorescent sensors for the Cu(II) have been prepared and reported [15-22].

The developed molecular sensors so far are commonly composed of two structural subunits: a fluorophore (for signal transduction) and an ionophore (for selective recognition of metal ion) [23-28]. Most of the reported Cu(II) fluorescent sensors, the binding of the metal ion causes a quenching of the fluorescence emission [29-35], due to its paramagnetic nature [36-38]. Furthermore, some of them are not good sensors because of the low sensitivity and high order of interference by chemically closely related metal ions [29-35].

Boradiazaindacene (BODIPY) fluorescent dyes have been widely used [39], because they have relatively high fluorescence quantum yields, good photo-stabilities, and absorption coefficients (Scheme 1) [40-42]. Herein, we chose BODIPY as the fluorophore and benzoyl isothiocyanate as receptor for selectively sensing Cu(II) in the environment.

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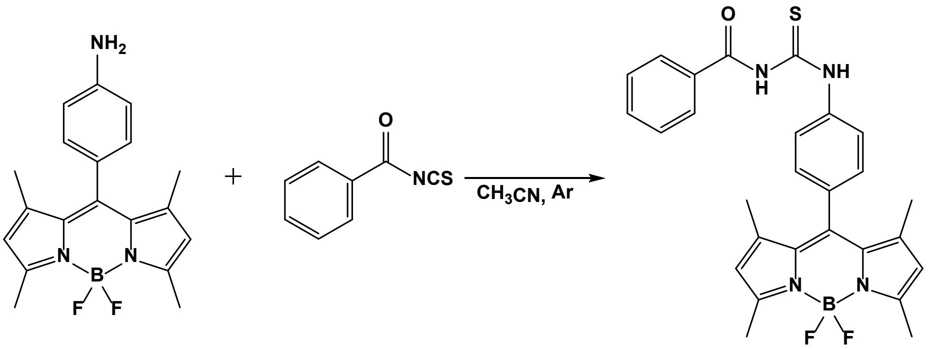

Scheme 1. Synthesis of sensor **1**.

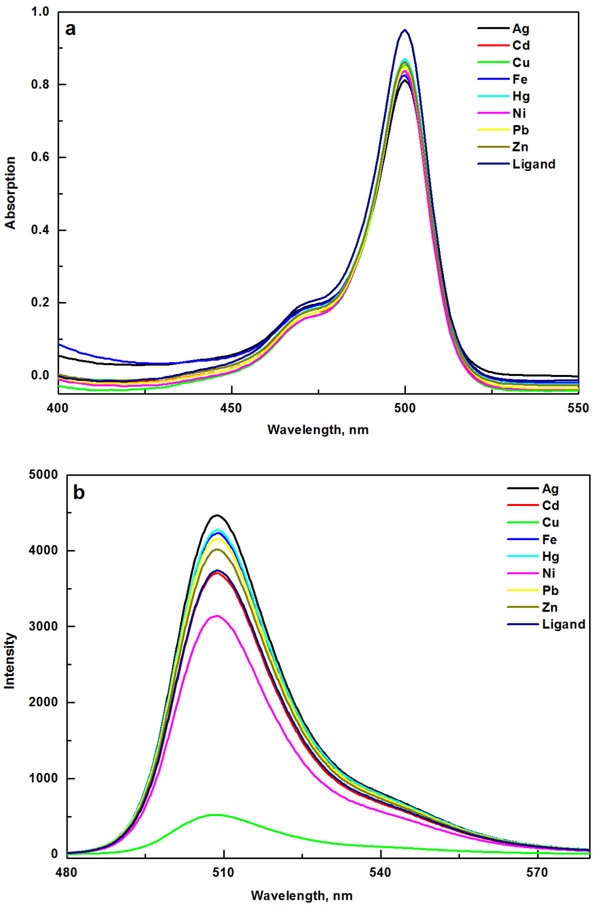

Figure 1. Absorption (a) and fluorescence spectra (b) of sensor **1** (10 uM) in ethanol:acetone (15:1, *v*:*v*) in the presence of Cu(II) and other metal ions (10 equivalents, respectively).

2. Experimental

2.1. Instrumentation

NMR experiments were performed with a JEOL AL-300 (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR) and the chemical shifts were recorded with respect to TMS as an internal reference. All fluorescence spectra were recorded on Hitachi FL-4500 spectrofluorimeter. The UV and fluorescence spectra of the prepared compound in the presence of $CuCl_2$, $HgCl_2$, $Cd(NO_3)_2$, $AgNO_3$, $Fe(NO_3)_3$, $Pb(OAc)_2{\cdot}3H_2O$, $ZnCl_2$, and $NiCl_2{\cdot}6H_2O$ in ethanol: acetone (15:1, *v*:*v*). Stock solutions (1.00 mM) of metal salts were prepared in ethanol. Stock solutions of Sensor **1** were prepared in tetrahydrofuran. Excitations were carried out at 470 nm with all excitation and emission slit widths of 5 nm. The total volume of all experiments was fixed at 2.0 mL except the titration.

2.2. Synthesis

Under nitrogen, a solution of 1,3,5,7-tetramethyl-8-(4'-aminophenyl)-4,4-difluoro-4-bora-3a, 4a-diaza-s-indacence (0.10 g, 0.3 mmol), benzoyl isothiocyanate (0.05 g, 0.3 mmol) in CH_3CN (10 mL) was stirred overnight, and then 30 mL $CHCl_3$ was added to it. The above solution was filtered, and the filtration was removed by rotary evaporation to produce a solid. The crude product was purified by the column chromatography (silica, CH_2Cl_2: hexane, 1:2, *v*:*v*) to give Sensor **1** (0.13 g).

N-((4-(5, 5-Difluoro-1, 3, 7, 9-tetramethyl-5H-4λ⁴, 5λ⁴-dipyrrolo[1, 2-c:2', 1'-f][1,3,2]diazaborinin-10-yl)phenyl)carbamothioyl)benzamide: Color: Orange. Yield: 86%. ^{1}H NMR (CDCl$_3$, 300 MHz, δ, ppm): 1.46 (s, 6H, CH$_3$), 2.56 (s, 6H, CH$_3$), 5.99 (s, 2H, pyrrole-H), 7.35 (d, *J* = 9 Hz, 2H, Ar-H), 7.58 (t, *J* = 9 Hz, 2H, Ar-H), 7.68 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.93 (t, *J* = 9 Hz, 4H, Ar-H), 9.14 (s, 1H, NH), 12.8 (s, 1H, NH). ^{13}C NMR (CDCl$_3$, 75 MHz, δ, ppm): 178.1 (1C, CO), 167.0 (1C, CS), 155.7 (1C, Ar-C), 143.1 (1C, Ar-C), 140.7 (2C, Ar-C), 138.4 (1C, Ar-C), 133.9 (2C, Ar-C), 133.2 (2C, Ar-C), 131.4 (2C, Ar-C), 129.3 (2C, Ar-C), 128.7 (2C, Ar-C), 127.5 (3C, Ar-C), 124.2 (2C, Ar-C), 121.3 (1C, Ar-C), 14.6 (4C, CH$_3$). HRMS (EI, *m/z*) calcd. for $C_{27}H_{25}BF_2N_4OS$ [M$^+$] 502.1810; found 502.1815.

3. Results and discussion

The fluorescent sensor **1** was prepared in one step from BODIPY and benzoyl isothiocyanate in CH$_3$CN with high yield (Scheme 1). The sensor **1** showed strong absorption at 500 nm and strong emission at 510 nm in ethanol:acetone (15:1, *v*:*v*), respectively. The UV and fluorescence changes of sensor **1** in presence of metal ions including Ag(I), Cd(II), Cu(II), Fe(III), Hg(II), Ni(II), Pb(II), and Zn(II) (10 equivalents) were studied in ethanol:acetone (15:1, *v*:*v*). As shown in Figure 1, there was little change in UV spectra of sensor **1** with and without metal ions. In the fluorescent spectra, however, the sensor **1** showed a strong fluorescence intensity at 510 nm, and could be quenched dramatically upon addition of Cu(II) ion (quenched 90%) due to the photo-induced electron transfer (PET) effect. Other metal ions showed negligible changes in ethanol:acetone (15:1, *v*:*v*). These results indicated that the selectivity of sensor **1** was good towards Cu(II) ion over other metal ions.

The competition experiment was also performed in ethanol: acetone (15:1, *v*:*v*) in Figure 2 (M bars: addition of 10 equivalents of Cu(II), Ag(I), Cd(II), Fe(III), Hg(II), Ni(II), Pb(II), and Zn(II) to the solution. Cu+M bars: addition of 10 equivalents of Ag(I)+Cu(II), Cd(II)+Cu(II), Fe(III)+Cu(II), Hg(II)+Cu(II), Ni(II)+Cu(II), Pb(II)+Cu(II), and Zn(II)+Cu(II) respectively, in ethanol: acetone (15:1, *v*:*v*)). All data (F) were normalized with respect to the emission of the free dye (F$_0$) at 510 nm. As shown in Figure 2, Fe(III), Hg(II) and Ni(II) showed a little interference and other metal ions showed little change in the presence of sensor **1** and Cu(II) ion.

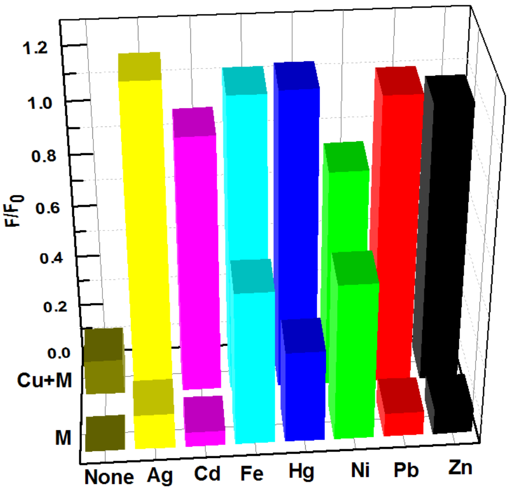

Figure 2. Fluorescence response of sensor **1** to various metal ions in ethanol:acetone (15:1, *v*:*v*), Bars represent the final integrated fluorescence response (F$_0$) over the initial integrated emission (F). M bars: only metal ion. Cu+M bars: Cu(II) and metal ion.

The titration and Job's plot spectra of sensor **1** in ethanol:acetone (15:1, *v*:*v*) with Cu(II) ion were illustrated in Figure 3. The fluorescence intensity of sensor **1** at 470 nm exhibited a gradual decrease with increasing the Cu(II) ion concentration from 0 and 4.5 μM. The inset shows the fluorescence titration profile of sensor **1** at 510 nm upon addition of Cu(II). The minimum point appeared at the mole fraction of 0.50 in a Job's plot, suggesting that the sensor **1** formed a 1:1 ligand-to-metal complex.

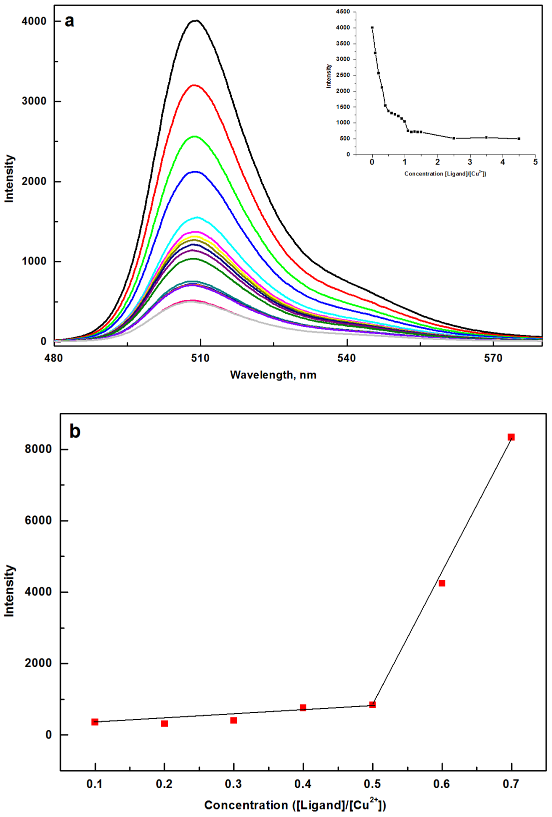

Figure 3. Fluorescence response of sensor **1** with Cu(II) concentrations between 0 and 4.5 equivalents (**a**) and Job's plot for sensor **1** with Cu(II) in ethanol: acetone (15:1, *v*:*v*) (**b**).

To examine the reversibility of sensor **1**, excess of triethanolamine was added to sensor **1** complex in ethanol: acetone (15:1, *v*:*v*). The solution showed strong fluorescence intensity after addition of triethanolamine (as shown in Figure 4), indicated that the sensor **1**-Cu(II) complex could be reversed by triethanolamine.

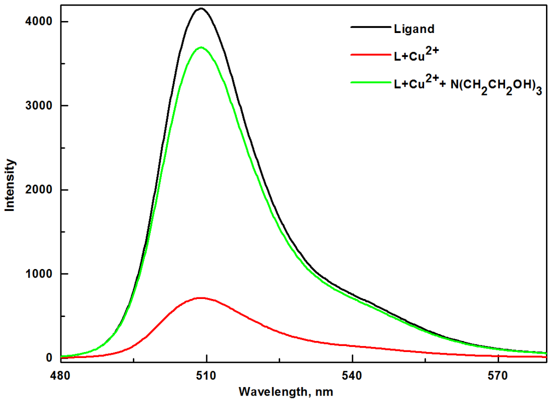

Figure 4. The reversibility of sensor **1** + Cu in presence of triethanolamine.

4. Conclusion

In conclusion, we demonstrated a simple fluorescent sensor for Cu(II) ion in ethanol: acetone (15:1, *v*:*v*). The selectivity towards Cu(II) ion is good over Ag(I), Cd(II), Fe(III), Hg(II), Ni(II), Pb(II), and Zn(II) ions, only Fe(III), Hg(II) and Ni(II) ions showed a little interference.

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Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.
Author contributions: All authors contributed equally to this work.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

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